(12) UK Patent Application (19) GB (11) 2 328 219 (13) A

(43) Date of A Publication 17.02.1999

(21) Application No 9814719.2

(22) Date of Filing 08.07.1998

(30) Priority Data
(31) 19730007 (32) 12.07.1997 (33) DE

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(51) INT CL[6]
C23C 10/06

(52) UK CL (Edition Q)
C7F FHB FP811 FR810 FR812 FR841 FR862 FR905

(56) Documents Cited
GB 2319261 A GB 2256876 A GB 1135015 A
EP 0731187 A1 EP 0064805 A2 US 5071678 A

(58) Field of Search
UK CL (Edition P) C7F FHB FHE
INT CL[6] C23C 10/06 10/08 10/10 10/12 10/14 16/06 16/08 16/10 16/12 16/14
Online: WPI

(54) Abstract Title
Process and apparatus for gas phase diffusion coating

(57) A process for diffusion coating of a workpiece 7 by transferring coating metal in the form of metal halide from a coating metal source 9a-c to the workpiece 7 where metal is deposited as a result of a chemical reaction. Gaseous reaction products return to the metal source 9a-c where further metal halide is formed and the cycle starts again. A temperature gradient between the workpiece 7 and coating metal source 9a-c, so that the latter is at as lower temperature, creates thermal convection which moves the gas within the reaction chamber. Apparatus in which this process may be performed includes a device 8 and 14 for producing the temperature gradient.

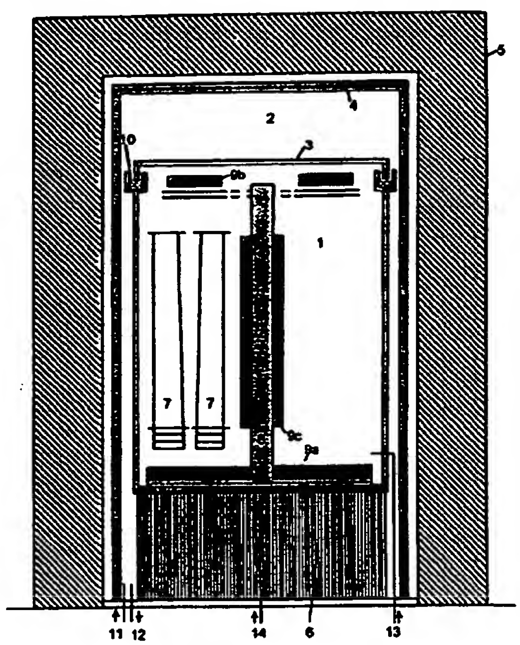

Fig. 1

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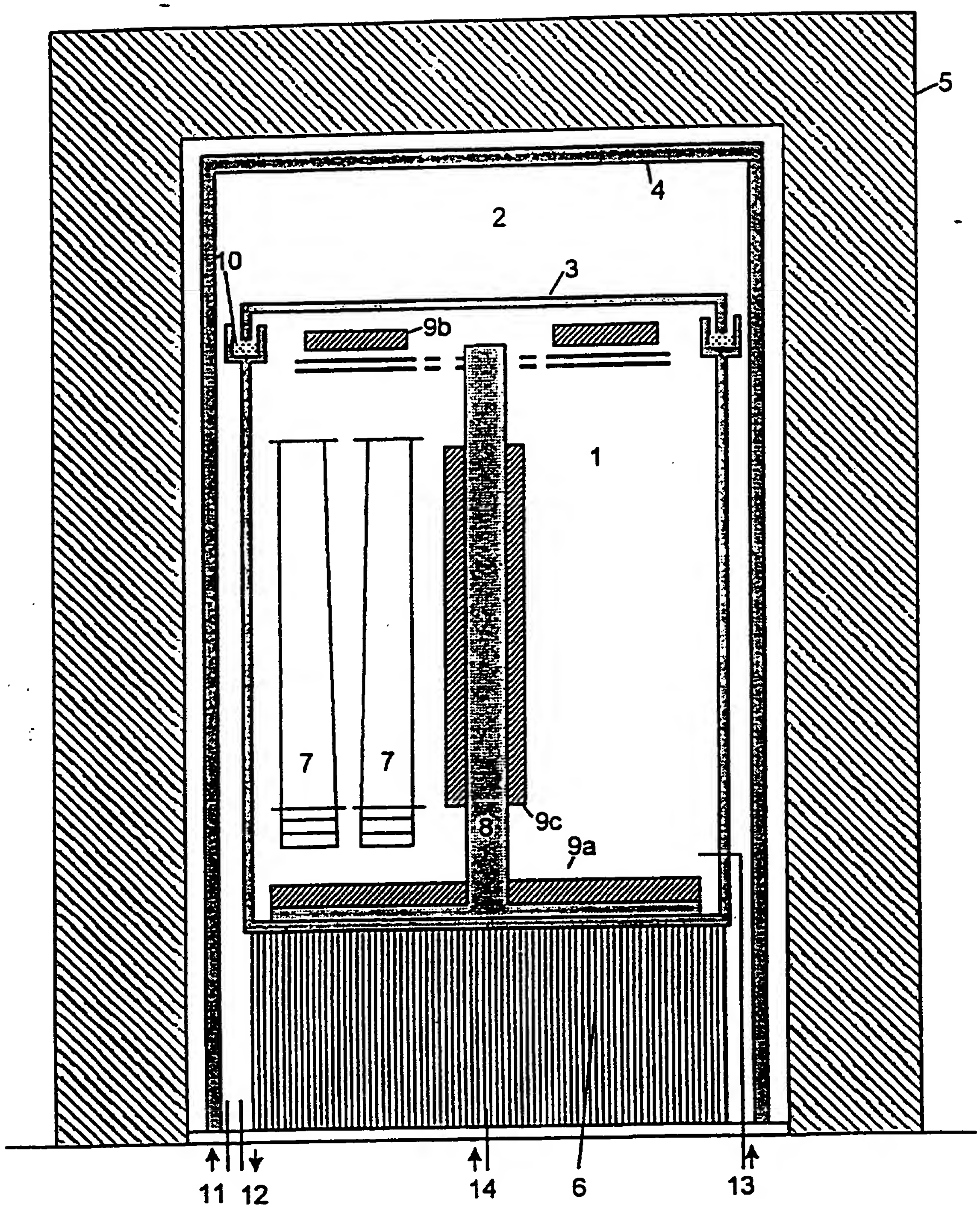

Fig. 1

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Process for the gas phase diffusion coating of workpieces of heat-resistant material with a coating material

The invention relates to a process for the gas phase diffusion coating of workpieces of heat-resistant material with a coating material.

In diffusion coating, a coating is applied to a workpiece in order to improve its surface properties, such as resistance to wear and resistance to corrosion. A layer of, for example, Al, Cr, Si is transferred to a workpiece which comprises, for example, an Ni, Co or Fe base alloy.

In the prior art, diffusion coating processes are known in which the coating is applied by means of powder packing. Such processes are known, for example, from US 3 667 985 for coating with AlTi and from US 3 958 047 for coating with Cr. Those processes are basically suitable for coating components of heat-resistant alloys uniformly and with high contents of Al and Cr, respectively. However, powder packing processes have certain inherent disadvantages, namely: the size of the powder packing to form a uniform layer is limited owing to problems of heat conduction. The donor powder in the powder packing is subject to sintering on the workpiece or produces unacceptable surface roughness by the incorporation of the powder into the layer. The handling of the powder is problematic from the environmental point of view owing to dust pollution and the disposal of the powder fraction mixtures. Furthermore, for example, EP 0 480 867 A2 and UK 1 135 015 disclose diffusion coating processes which operate without powder packing. Both known processes have

the disadvantage, however, that the reaction for donor gas formation and for deposition operate in a thermodynamically unfavourable manner owing to the type of apparatus and the geometrical arrangement of the workpiece and the donor source. Further disadvantages are that coating processes, compared with the powder packing process, produce a layer having a smaller thickness or a lower content of diffusing elements. Finally, one disadvantage is that, if the donor gas source is arranged upstream of the reaction chamber, expensive additional devices which are susceptible to failure are necessary to obtain a reactive gas mixture.

The problem of the invention is to provide a process for gas phase diffusion coating of the type required which is capable of producing uniform diffusion layers even on large workpiece surfaces and which is free from the above-mentioned disadvantages of the known processes. The invention is also to provide an apparatus for carrying out the process.

According to the invention, the problem set is solved by a process for the gas phase diffusion coating of workpieces of heat-resistant material with a coating material, the coating material being transferred according to the invention in the form of a metal halide onto the workpiece from a coating material source by means of a metal halide circuit.

A substantial advantage of the process according to the invention is that uniform smooth layers having a high surface quality can be produced. A further advantage of the process according to the invention is that even bulky workpieces can be coated. Another advantage of the process

according to the invention is that layers having a large layer thickness and a high boundary layer content of elements to be transferred can be produced.

According to a development of the invention, it is provided that the metal halide is produced in the coating material source which contains a metal.

It is advantageously provided that the metal halide is produced by introducing a halide-containing gas into the coating material source which contains a metal.

Alternatively, it is of special advantage if the metal halide is produced by a decomposition reaction of a halide-containing, preferably pulverulent, solid body contained in the coating material source.

The coating material source advantageously contains the metal in the form of a powder or granules.

According to an especially advantageous embodiment of the invention, it is provided that a temperature gradient is produced between the workpiece to be coated and the coating material source, so that the workpiece is at a higher temperature than the coating material source.

It is advantageously provided that the workpieces and the coating material source are arranged in a heatable reaction container and that the temperature gradient is produced by removing heat from the coating material source.

According to an especially advantageous form of the process according to the invention, it is provided that the metal halide circuit is a closed circuit between the coating material source and the workpiece.

The closed circuit is advantageously driven by thermal convection.

The coating operation is advantageously effected in an inert gas atmosphere at elevated temperature.

The inert gas atmosphere advantageously contains argon gas and/or hydrogen gas.

Advantageously, the inert gas atmosphere is produced during heating to the elevated temperature.

It is of particular advantage if, during the heating operation, argon is supplied as the inert gas at relatively low temperatures, preferably up to approximately 700°C, and if hydrogen is supplied as the inert gas at relatively high temperatures, preferably above 700°C.

The inert gas atmosphere advantageously contains less than 100 ppm of oxygen and less than 100 ppm of steam.

The coating operation is advantageously carried out at an elevated temperature of approximately from 1000°C to 1200°C, preferably between 1080°C and 1140°C.

The metal is an elemental or molecular substance or a corresponding substance mixture that forms a metal halide with a halide.

The substance is advantageously Al, Cr, Si or a compound or mixture thereof.

The substance or substance mixture is advantageously in the form of granules or a powder.

It is especially advantageous if the granules or powder contain(s) a halide in the form of a pulverulent or granular solid body.

According to the invention, an apparatus is also provided for the gas phase diffusion coating of workpieces of heat-resistant material with a coating material by the process according to the invention, which apparatus is characterised by:

- a heatable reaction container for receiving the workpieces to be coated,

- a device for producing a metal halide, and

- a device for producing a temperature gradient between the workpiece to be coated and the device for producing the metal halide.

According to an advantageous development of the apparatus according to the invention it is provided that the device for producing the metal halide contains at least one donor

container for receiving metal used for producing the metal halide.

It is advantageous to provide a device for supplying halide-containing gas to the donor container.

According to an especially advantageous development of the apparatus according to the invention, it is provided that the device for producing a temperature gradient contains a cooling arrangement coupled thermally to the device for producing the metal halide.

Advantageously, the cooling arrangement is cooled by a cooling gas.

It is especially advantageous if the cooling arrangement contains a lamellar or tube arrangement through which the cooling gas flows.

The cooling arrangement is advantageously coupled thermally to the device for producing the metal halide by way of a heat-conducting device.

According to an advantageous development of the apparatus according to the invention:

- a retort container which surrounds the reaction container and which has a retort chamber surrounding the reaction container,

- a heating device for heating the retort contain r and therefore the reaction container, and

- a semi-gas-permeable blocking device, arranged between the inner chamber of the reaction container and the retort chamber, for the selective delivery of excess gases from the inner chamber of the reaction container into the retort chamber,

are provided.

It is advantageously provided that the semi-gas-permeable blocking device is formed by a labyrinth-pored or open-pored cavity arrangement provided in the wall of the reaction container.

It is especially advantageous to provide the apparatus according to the invention with several donor containers of which at least one donor container is maintained at a first, lower temperature level and at least one second and/or third donor container is/are maintained at a higher temperature level, the temperature levels of the donor containers being lower than the temperature level of the workpieces to be coated.

The different temperature levels of the donor containers are advantageously brought about by different thermal coupling thereof to the cooling arrangement by means of the temperature gradient device.

Embodiments of the invention are described hereinafter with reference to the drawing.

Figure 1 shows diagrammatically a cross-section through an apparatus for effecting a process for the gas phase diffusion coating of workpieces of heat-resistant material with a coating material according to the present invention.

The Figure shows diagrammatically a section through an apparatus for effecting the gas phase diffusion coating process according to the invention. A reaction container 3 forms a reaction chamber 1 in which the gas phase diffusion coating operation takes place. The reaction container 3 is surrounded by a retort container 4 which surrounds a retort chamber 2. The retort chamber 2 surrounds the reaction container 3, at least partially. The retort container 4 is for its part surrounded by a heating system 5 which is formed by a furnace.

The workpieces 7 to be coated, of which two are shown diagrammatically in the Figure, are arranged in the reaction chamber 1. A device for producing a metal halide is formed by several donor containers 9a, 9b, 9c which are arranged at different sites within the reaction chamber 1. Arranged on the underside of the reaction container 3 is a cooling arrangement 6 which is formed by a heat-conducting lamellar or tube construction through which flows a cooling gas supplied by way of a cooling gas line 14. A heat-conducting device 8 is provided in heat contact with the cooling arrangement 6 <u>via</u> the base of the reaction container 3 and is formed by a base portion and an upright portion. First donor containers 9a are coupled thermally to the base portion of the heat-conducting device 8, whereas third donor containers 9c are coupled thermally to the upright portion of the heat-conducting device 8; second donor containers 9b

are arranged in the upper portion of the reaction container 3.

A semi-gas-permeable blocking device 10 is provided in the wall of the reaction container 3.

The reaction chamber 1 is brought to elevated temperature by the heating system 5 indirectly by way of the reaction container 3, the retort container 4 surrounding the latter, and the retort chamber 2. The cooling gas flowing through the cooling arrangement 6 cools the cooling arrangement 6 and, directly via the base of the reaction container 3, the base portion of the heat-conducting device 8 and the upright portion thereof and therefore the donor containers 9a and 9c, so that a temperature gradient is created between the workpieces 7 to be coated and the donor containers 9a and 9c such that the workpieces 7 are at a higher temperature than are the donor containers 9a and 9c.

The semi-gas-permeable blocking device 10 enables excess or expanding gas or specifically lighter reaction gases to escape from the reaction chamber 1 into the retort chamber 2 but prevents gases from entering the reaction chamber 1 from the retort chamber 2 by means of a suitable labyrinth-pored or open-pored tube construction. Lines 11 and 12 are used to supply and remove gases into and out of, respectively, the retort chamber, and a line 13 is used to supply gas to the reaction chamber 1. Inert gases or reducing gases are conveyed to or removed from the retort chamber 2 via the lines 11, 12; inert gases, reducing gases or halide-containing gases are conveyed into the reaction chamber 1 via the line 13.

The gas phase diffusion coating process is divided in terms of time into the spheres start, heating operation with supply of inert gases, hold cycle and cooling operation. At the start of the process, the reaction chamber 1 and the retort chamber 2 are freed from the normal atmosphere by the supply of inert gas at room temperature to such an extent that the oxygen concentration and the steam concentration are below 100 ppm. For example, argon and/or hydrogen gas are/is used as the inert gas. During the heating operation, the formation of the metal halide(s) responsible for coating is set in train at least in the donor metal containers 9a by supplying halide-containing gas or by the decomposition reaction of a halide-containing, preferably pulverulent, solid body. Examples of the formation of such metal halides are:

$$2\ HCl + Cr \Leftrightarrow CrCl_2 + H_2 \qquad (1)$$

$$AlF_3 + 2Al \Leftrightarrow 3\ AlF \qquad (2)$$

Excess HCl and H_2, as gas compounds that are specifically lighter than the metal halides, are removed from the reaction chamber 1 <u>via</u> the semi-gas-permeable blocking device 10.

Owing to thermal convection, the metal halides rise at the outside of the reaction container 3 and fall again in the region of the middle of the reaction chamber 1 in the vicinity of the upright portion of the heat-conducting device 8 <u>via</u> the donor metal containers 9c and 9a. Thus a gas circuit is formed which is induced by the temperature gradients produced by the cooling arrangement 6 in co-operation with

the heat-conducting device 8. In addition to the thermal convection, the gas circuit is aided by the deposition reaction of the metal halides on the workpieces 7. The main reactions taking place may be, for example:

$3\ MeHal_2 + Ni_{workpiece}$	$\Leftrightarrow$	$MeNi + 2\ MeHal_3$	(A1)
$3\ MeHal + Ni_{workpiece}$	$\Leftrightarrow$	$MeNi + MeHal_3$	(A2)
$MeHal_2 + H_2 + Ni_{workpiece}$	$\Leftrightarrow$	$MeNi + 2\ HHal$	(B1)
$2\ MeHal_2 + H_2 + 2Ni_{workpiece}$	$\Leftrightarrow$	$2\ MeNi + 2\ HHal$	(B2)

The HHal produced in reactions B1 and B2 is removed by way of the donor metal containers 9b, monovalent and divalent metal halides being produced in the induced circuit process from the trivalent metal halides at the donor containers.

The reactions of the monovalent and divalent metal halides are promoted by the relatively low temperatures in the region of the donor metal containers because the reactions are exothermic and these are preferred thermodynamically at relatively low temperatures. In contrast, the deposition reactions, which are endothermic, or are exothermic to a far lesser extent than are the above-mentioned reactions on the surfaces of the workpieces 7, are promoted by a specifically higher temperature.

Thus, there is produced in the reaction chamber 1 a physically induced closed circuit process with thermodynamically promoted high proportions or activities of metal-yielding metal halides with close contact between the donor and the consumer of the metal to be deposited. In that manner, very uniform diffusion coatings having high boundary layer

contents of, for example, Al or Cr are produced ov r th workpiece 7.

After a holding time of from 2 to 20 hours at process temperature, the reaction chamber 1 is flushed free from reactive halides by the introduction of inert gas and cooled.

The coating operation takes place at an elevated temperature of approximately from 1000°C to 1200°C, preferably between 1080°C and 1140°C.

Example 1

In Example 1, the gas phase diffusion coating process according to the invention is used to diffusion-coat turbine blades, which are produced from the alloy Mar-M-247 and which are 710 mm long, with a chromisation layer 70 µm thick.

From 10 to 24 blades are charged into the reaction chamber 1. 54 kg of Cr granules with, in addition, 540 g of ammonium chloride, uniformly mixed, are provided in the donor metal bodies 9a, 9b and 9c. The reaction container 3 and the retort chamber 2 are flushed for at least 30 minutes with argon at a throughput rate of 2 m^3/h. Heating is effected over a period of 2.5 hours to 1140°C, argon being introduced at 0.5 m^3/h up to a temperature of 700°C. At high temperature, there is a temperature difference between the workpieces 7 and the donor metal bodies 9a, 9b, 9c of up to 30 K. The holding time is 14 hours. A typical diffusion

layer produced by th process according to Example 1 has a Cr content of 28% by weight.

Example 2

In Example 2, the process according to the invention is used to coat turbine blades produced from the nickel base alloy Rene 80 with an aluminium diffusion layer of 80 µm. Up to 32 turbine blades are arranged in a plane of the reaction container. 48 kg of AlCr granules with 50% by weight of Al and 320 g of AlF_3 as the halogen donor are provided in the donor containers 9a, 9b, 9c. Up to 700°C, the reaction chamber 1 is flushed at 2 m^3/h and at from 700°C to 1000°C the reaction chamber 1 is flushed with H_2.

Coating takes place at a high temperature of 1080°C for a holding period of 4.5 hours. The result was a layer thickness of from 65 to 85 µm and 33% by weight of Al in the surface.

Patent Claims

1. Process for the gas phase diffusion coating of workpieces of heat-resistant material with a coating material, characterised in that the coating material is transferred in the form of a metal halide onto the workpiece from a coating material source by means of a metal halide circuit.

2. Process according to claim 1, characterised in that the metal halide is produced in the coating material source which contains a metal.

3. Process according to claim 2, characterised in that the metal halide is produced by introducing a halide-containing gas into the coating material source which contains a metal.

4. Process according to claim 2, characterised in that the metal halide is produced by a decomposition reaction of a halide-containing, preferably pulverulent, solid body contained in the coating material source.

5. Process according to claim 2, 3 or 4, characterised in that the coating material source contains the metal in the form of a powder or granules.

6. Process according to any one of claims 1 to 5, characterised in that a temperature gradient is produced between the workpiece to be coated and the coating material source so that the workpiece is at a higher temperature than the coating material source.

7. Process according to claim 6, characterised in that the workpieces and the coating material source are arranged in a heatable reaction container and the temperature gradient is produced by removing heat from the coating material source.

8. Process according to any one of claims 1 to 7, characterised in that the metal halide circuit is a closed circuit between the coating material source and the workpiece.

9. Process according to any one of claims 1 to 8, characterised in that the closed circuit is driven by thermal convection.

10. Process according to any one of claims 1 to 9, characterised in that the coating operation is effected in an inert gas atmosphere at elevated temperature.

11. Process according to claim 10, characterised in that the inert gas atmosphere contains argon gas and/or hydrogen gas.

12. Process according to claim 10 or 11, characterised in that the inert gas atmosphere is produced during heating to the elevated temperature.

13. Process according to claim 12, characterised in that, during the heating operation, argon is supplied as the inert gas at relatively low temperatures, preferably up to approximately 700°C, and hydrogen is supplied as the inert gas at relatively high temperatures, preferably above 700°C,.

14. Process according to any one of claims 10 to 13, characterised in that the inert gas atmosphere contains less than 100 ppm of oxygen and less than 100 ppm of steam.

15. Process according to any one of claims 1 to 14, characterised in that the coating operation is carried out at an elevated temperature of approximately from 1000°C to 1200°C, preferably between 1080°C and 1140°C.

16. Process according to any one of claims 1 to 15, characterised in that the metal is an elemental or molecular substance or substance mixture that forms a metal halide with a halide.

17. Process according to claim 16, characterised in that the substance or substance mixture is Al, Cr, Si or a compound or mixture thereof.

18. Process according to claim 16 or 17, characterised in that the substance or substance mixture is in the form of granules or a powder.

19. Process according to claim 18, characterised in that the granules contain a halide in the form of a pulverulent or granular solid body, preferably ammonium chloride or AlF_3.

20. Apparatus for the gas phase diffusion coating of workpieces of heat-resistant material with a coating material by the process according to any one of claims 1 to 19, characterised by:

- a heatable reaction container for receiving the workpieces to be coated,

- a device for producing a metal halide, and

- a device for producing a temperature gradient between the workpieces to be coated and the device for producing the metal halide.

21. Apparatus according to claim 20, characterised in that the device for producing the metal halide contains at least one donor container for receiving metal used for producing the metal halide.

22. Apparatus according to claim 21, characterised in that a device for supplying halide-containing gas to the donor container is provided.

23. Apparatus according to claim 20, 21 or 22, characterised in that the device for producing a temperature gradient contains a cooling arrangement coupled thermally to the device for producing the metal halide.

24. Apparatus according to claim 23, characterised in that the cooling arrangement is cooled by a cooling gas.

25. Apparatus according to claim 24, characterised in that the cooling arrangement contains a lamellar or tube arrangement through which the cooling gas flows.

26. Apparatus according to claim 23, 24 or 25, characterised in that the cooling arrangement is coupled thermally to

the device for producing the metal halide by way of a heat-conducting device.

27. Apparatus according to any one of claims 20 to 26, characterised by

- a retort container which surrounds the reaction container and which has a retort chamber surrounding the reaction container,

- a heating device for heating the retort container and therefore the reaction container, and

- a semi-gas-permeable blocking device, arranged between the inner chamber of the reaction container and the retort chamber, for the selective delivery of excess gases from the inner chamber of the reaction container into the retort chamber.

28. Apparatus according to claim 27, characterised in that the semi-gas-permeable blocking device is formed by a labyrinth-pored or open-pored cavity arrangement provided in the wall of the reaction container.

29. Apparatus according to any one of claims 21 to 28, characterised in that several donor containers are provided of which at least one donor container is maintained at a first, lower temperature level and at least one second and/or third donor container is/are maintained at a higher temperature level, the temperature levels of the donor containers being lower than the temperature level of the workpieces to be coated.

30. Apparatus according to claim 29, characterised in that the different temperature levels of the donor containers are brought about by different thermal coupling thereof to the cooling arrangement by means of the temperature gradient device.

The Patent Office

20.

Application N : GB 9814719.2
Claims searched: 1-30

Examiner: Matthew Lawson
Date of search: 24 September 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C7F (FHB, FHE)

Int Cl (Ed.6): C23C 10/06, 10/08, 10/10, 10/12, 10/14, 16/06, 16/08, 16/10, 16/12, 16/14

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
A	GB 2319261 A	(NEW AMERICAN) page 3 lines 8-17.	
X	GB 2256876 A	(MTU) the whole document, in particular figure 1.	1-3,5,10-12,14-18, 20-22
X	GB 1135015	(SOCIÉTÉ) the whole document, in particular page 3 lines 118-122 and fig 2.	1-3,5,6, 10-12,14-18,20-22
X	EP 0731187 A1	(TURBINE) column 5 line 21 - column 6 line 14 and figure 2.	1-6,8,10-12,14-19
X	EP 0064805 A2	(FUJITSU) page 7 line 33 - page 48 line 12 and figure 2.	1-3,10-12, 14,16,17, 20-22
X	US 5071678	(GRYBOWSKI) the whole document, in particular the figures.	1-3,5,10-12,14-18

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